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(54) **Polyolefin materials having enhanced surface durability and methods of making the same by exposure to radiation**

(57) The invention relates to thermoplastic polyolefin compositions having enhanced surface durability and products thereof which include a thermoplastic polyolefin base component at least one radiation-polymerizable component present in an amount sufficient to enhance the surface durability of the thermoplastic polyolefin component when radiation-cured and at least one photoinitiator present in an amount sufficient to initiate crosslinking of the radiation-polymerizable component

upon exposure of the thermoplastic polyolefin composition to radiation. The invention further relates to methods of providing a cured thermoplastic polyolefin composition having enhanced surface durability by preparing a mixture having a thermoplastic polyolefin base component, at least one radiation-polymerizable component, and at least one photoinitiator, and then exposing the thermoplastic polyolefin composition to radiation thereby providing a thermoplastic polyolefin composition having enhanced surface durability.

EP 0 921 152 A2

Description

[0001] This invention relates to thermoplastic, polyolefin materials ("polyolefins") having superior mar, scratch, wear, and abrasion resistance and methods of making such polyolefins by exposure to radiation to crosslink unsaturated polyolefins therein.

[0002] Polyolefins are useful in a wide variety of applications due to their strength, environmental resistance and moldability. Many polyolefins are too easily scratched, marred, worn, abraded or otherwise damaged on their surface. These surface characteristics may be measured in a variety of ways. For example, scratch resistance may be measured by vertically penetrating a scratch needle, with a spherical tip into a polyolefin or other material surface under a constant load. The needle is then moved horizontally at a constant rate, and the width and/or depth of any formed scratch is measured (see, e.g., T. Nomura, et al., *J. Applied Polymer Sci.* 55:1307-1315 (1995)). Generally, it is desired to enhance the service life of a polyolefin by improving these surface characteristics to reduce scratching, marring, wearing, abrasion, and the like.

[0003] One conventional method to enhance surface characteristics is to use inorganic particulate material, such as various silicas. Uniform dispersion of these particulates is difficult to achieve, however, and this results in non-uniform surface properties in such products. The use of these particulates also tends to damage other desirable physical properties of the polyolefin, resulting in loss of impact strength, toughness, processability, and the like.

[0004] A more effective conventional method of providing surface enhancing characteristics to certain polyolefins is disclosed in U.S. Patent No. 4,921,669. This patent discloses passing a web of extruded thermoplastic synthetic resin through a polishing roll stack, wherein at least one of the rolls has thereon a film of a material forming such a scratch resistant coating that is transferred from the roll to the web surface. Such conventional methods of enhancing the surface characteristics of a polyolefin require expensive, bulky equipment that also increase the processing time of polyolefin products.

[0005] Another way to enhance surface characteristics of polyolefins is described in U.S. Patent No. 4,000,216, which discloses an extrudable, moldable, or heat formable blend of a thermoplastic polymer and a surface altering agent of at least one monoethylenically unsaturated monomer for said thermoplastic polymer, wherein the surface altering agent has cross-linked polymer particles having an average size of 1 to 30 microns. The surface altering agent is preferably prepared by an endopolymerization, which is used with a compatible polyolefin to be altered.

[0006] Another conventional way to enhance surface characteristics of various articles is to apply acrylic polymers or coatings to an article and subsequently cure the polymer or coating with a radiation source, such as ultraviolet radiation ("UV"). The following patents describe a variety of examples of such conventional "apply coating and cure" methods and compositions.

[0007] U.S. Patent Nos. 4,153,526 and 4,039,720 disclose safety glass made by laminating a saturated polyvinyl acetal film and a photoinitiator to a ply of glass, and irradiating the film with UV to initiate crosslinking and to provide improved solvent-abrasion resistance.

[0008] U.S. Patent No. 4,227,979 discloses radiation-curable coating compositions including one or more amide acrylate compounds that form mar-resistant protective and decorative film coatings.

[0009] U.S. Patent No. 4,255,303 discloses a composition for coating electrical applications including ethylene polymer and at least 10 parts by weight of talc filler per 100 parts by weight of polymer, where the talc is coated with at least one metallic salt of a fatty acid having 8 to 20 carbon atoms. The ethylene polymers may be curable by irradiation with high-energy electron beams or a chemical curing agent, such as organic peroxide.

[0010] U.S. Patent No. 4,371,566 discloses actinic radiation curable coating compositions for application to many substrates having a pentaerythritol-based polyacrylate or polymethacrylate, such as pentaerythritol tetraacrylate, a vinyl chloride-vinyl acetate containing polymer, and a photoinitiator, preferably applied by spraying a solution onto the substrate.

[0011] U.S. Patent No. 4,478,876 discloses a process of coating a solid substrate with an abrasion resistant silicone hard coating curable upon UV exposure under a non-inert atmosphere, such as air. The composition includes a UV crosslinkable polyfunctional acrylate monomer, SiO₂ in the form of colloidal silica, and acryloxy functional silanes and a selected blend of ketone-type and photoinitiators.

[0012] U.S. Patent No. 4,814,207 discloses a method for applying a scratch and weather resistant film coating to a shaped article by applying to the article a thin film of a mixture of free radically polymerizable monomer having at least two polymerizable olefinic bonds, a peroxide initiator having a half life of less than two minutes at 100°C, and an ultraviolet stabilizer, and curing the film by heating it to a temperature greater than 70°C.

[0013] U.S. Patent No. 4,902,578 discloses a radiation-curable coating for thermoplastic substrates having a polyfunctional acrylic monomer, a mono-, di-, or trifunctional acrylic monomer, a thermoplastic or elastomeric polymer, and a photoinitiator.

[0014] U.S. Patent No. 5,006,436 discloses a UV curable, aqueous alkaline developable solder mask composition having a thermal free radical initiator capable of generating free radicals with heat, and a polyunsaturated compound

capable of being thermally cross-linked by the free radicals to provide a substantially fully cured coating.

[0015] U.S. Patent No. 5,316,791 discloses a process for improving the impact resistance of a coated plastic substrate by applying an aqueous polyurethane dispersion as a primer layer, partially curing the layer by air drying, applying a coating composition over the primer layer, and curing the coating composition to form an abrasion-resistant hard coat.

[0016] U.S. Patent No. 5,382,604 discloses a crosslinked adhesive composition having an epoxidized diolefin block polymer crosslinked by UV radiation through at least some of the epoxy functionality.

[0017] U.S. Patent No. 5,558,911 discloses a method of coating articles with powder coatings having polymers applied to the substrate to be coated, melting the polymers, and crosslinking by UV radiation.

[0018] U.S. Patent No. 5,591,551 discloses a lithographic coating and method of coating at least a portion of a surface of an article with a radiation-crosslinkable polymer and exposing it to a pattern of radiation to produce an image. The polymer is disclosed to be a copolymer of an isoolefin of 4-7 carbon atoms and para-alkylstyrene.

[0019] U.S. Patent No. 5,618,586 discloses self-crosslinkable film-forming compositions as coatings and a process for preparing multi-layered coated articles with a colored base coat and a clear top coat, wherein the composition includes a non-gelled addition polymer that is the free radical initiated reaction product of an N-alkoxymethyl(meth)acrylamide and at least one other ethylenically unsaturated monomer.

[0020] These conventional curable products generally require several steps, particularly coating or effectively laminating a prepared product with the UV-curable coating. However, it would be advantageous to provide independent polyolefin compositions that are capable of being cured without the need for additional processing steps, such as coating or laminating an article with a curable composition. It is thus desired to produce such a product, preferably one having enhanced surface durability. The present invention provides new polyolefin compositions that satisfy this need.

[0021] The present invention relates to a thermoplastic polyolefin composition having enhanced surface durability, which includes (a) a base component of a thermoplastic polyolefin, (b) at least one radiation-polymerizable component, present in an amount to enhance the surface durability of the thermoplastic polyolefin base component when radiation-cured, and (c) at least one photoinitiator present in an amount sufficient to initiate crosslinking of the radiation-polymerizable component upon exposure of the thermoplastic polyolefin composition to radiation.

[0022] In one embodiment, the polyolefin composition also includes a filler (d) in an amount of between 0.1 to 30 weight percent. In a preferred embodiment, the filler includes calcium carbonate, clay, talc, mica, glass, zinc oxide, wollastonite, silica, titanium dioxide, or mixtures thereof.

[0023] In another embodiment, the thermoplastic polyolefin base component is thermally treated prior to or subsequent to radiation exposure. The thermal treatment may vary in intensity from 25°C to 150°C and may vary in duration from a few minutes up to a few days (e.g., from 2 minutes to 48 hours) depending on the temperature and desired extent of cure. Alternately, the base component can be subjected to a series of alternating thermal and radiation treatments which may be of varying duration lengths depending on the desired physical properties.

[0024] The compositions may contain photo-oxidative stabilizers that prevent environmental degradation of the thermoplastic polyolefin base component without interfering substantially with the photoinitiated surface crosslinking.

[0025] The thermoplastic polyolefin base component (a) may include a blend of a crystalline or semi-crystalline poly- α -olefin and an amorphous poly- α -olefin. In a preferred embodiment, the thermoplastic polyolefin base component includes a blend of semi-crystalline polypropylene and amorphous ethylene copolymerized with a poly- α -olefin. In another embodiment, the amorphous poly- α -olefin includes amorphous ethylene and at least one diene. Generally, the thermoplastic polyolefin base component is present in an amount of about 99 to 55 weight percent of the composition. In a preferred embodiment, the thermoplastic polyolefin base component is present from about 95 to 65 weight percent of the composition.

[0026] The radiation-polymerizable component (b) may include an unsaturated polyolefin. In a preferred embodiment, the unsaturated polyolefin includes an ethylene, propylene and diene terpolymer; polybutadiene; polyisoprene; a styrenic polymer; an ethylene and propylene copolymer; or mixtures thereof. Typically, the radiation-polymerizable component is present in an amount of about 1 to 30 weight percent of the thermoplastic polyolefin composition.

[0027] The photoinitiator (c) may be any one of benzoin and benzoin ether derivatives; benzil ketal derivatives; α,α -dialkoxyacetophenone derivatives; α -aminoalkylphenone derivatives; α -hydroxyalkylphenone derivatives; mono-, bis- or trisacylphosphine oxides; mono-, bis- or trisacylphosphine sulfides; phenylglyoxalate derivatives; O-acyl-2-oximino ketone derivatives; benzophenone and its derivatives; Michler's ketone and its derivatives; thioxanthone and its derivatives; as well as mixtures thereof; and all the polymer-bound compounds of the type mentioned above. In a preferred embodiment, the photoinitiator is selected from benzil ketal derivatives and mono- or bisacylphosphine oxides. The photoinitiator is typically present in an amount of about 0.01 to 5 weight percent of the composition. It is possible to use one photoinitiator alone, but also mixtures of photoinitiators may be used, optionally along with accelerators that facilitate rapid crosslinking.

[0028] The invention also relates to a method of providing a cured thermoplastic polyolefin composition having enhanced surface durability by (1) preparing a mixture of (a) a thermoplastic polyolefin base component, (b) at least one radiation-polymerizable component in an amount sufficient to enhance the surface durability of the thermoplastic poly-

olefin component when radiation cured, and (c) at least one photoinitiator in an amount sufficient to facilitate crosslinking of the radiation-polymerizable component when the thermoplastic polyolefin composition is exposed to radiation, and (2) then exposing a surface of the thermoplastic polyolefin composition to radiation in an amount sufficient to crosslink the radiation-polymerizable component at least at the exposed surface, thereby providing a thermoplastic polyolefin composition having enhanced surface durability.

[0029] In one embodiment, the radiation is selected to be ultraviolet, electron beam, gamma, visible, microwave, infrared, or thermal radiation, or mixtures thereof. In another embodiment the radiation is imparted at a power of 0.1 J/cm² and above and at a wavelength between about 200 to 500 nm.

[0030] In a preferred embodiment, the thermoplastic polyolefin base component (a) is selected to be a blend of a crystalline or semicrystalline poly- α -olefin and an amorphous poly- α -olefin, the radiation-polymerizable (b) component is selected to be an unsaturated polyolefin that is present in about 0.01 to 20 weight percent of the composition, the photoinitiator (c) is selected to be benzil ketals or mono-, bis- or trisacylphosphine oxides present in about 0.1 to 5 weight percent of the composition, and a filler (d) is added to the mixture. The method may further include forming the thermoplastic polyolefin composition into a desired shape prior to exposing the surface of the composition to the radiation.

[0031] The invention also relates to a thermoplastic polyolefin composition having enhanced surface durability formed by the above-described method. In one embodiment, the composition has an outer surface that contains a polymerized component so that the surface scratch resistance after irradiation has a rating of 1.5 or lower on the Solvay scale (see definition below) after cure.

[0032] Polyolefin compositions having enhanced surface durability, and a process for making the same, have now been advantageously discovered. The polyolefin compositions of the present invention include (a) a thermoplastic polyolefin base component, (b) a radiation-polymerizable component, and (c) a photoinitiator, together with one or more optional fillers (d) used to create a final product having desired characteristics. The present invention is believed to influence the mechanics of surface deformation and recovery by preferentially introducing crosslinks near the surface of a formed article made from the polyolefin composition. Thus, the polyolefin compositions according to the invention exhibit superior durability and resistance to marring, scratching, wear, abrasion, and other surface damage without the need for a cumbersome coating-type process.

[0033] The terms "thermoplastic polyolefin composition" or "polyolefin composition" are intended to include any composition that contains one or more crystalline or semi-crystalline olefin polymers, such as polyethylene, polypropylene or other C₅-C₂₀ olefins. The crystallinity of such olefins can range from 30 to 100%. Mixtures of these polymers are contemplated as part of the invention, as well. Other components that typically can be included in such polyolefin compositions are amorphous polymers of C₃-C₂₀ olefins, whether used alone or as co-polymers of two different olefins or as terpolymers of three different olefins. Such amorphous components are typically added to enhance the low temperature impact or paintability properties of the polyolefin composition. For example, the polymer composition of U.S. Patents 4,945,005, 4,997,720 and 5,498,671 can be used as the polyolefin component (a) in this invention.

[0034] The polyolefin compositions of the invention may include any thermoplastic polyolefin base component of one or more polyolefins that do not crosslink but that have compatibility with one or more unsaturated polyolefins that are capable of crosslinking under irradiation, although the polyolefin base component is preferably a polyolefin, more preferably a blend of a crystalline or semi-crystalline poly- α -olefin and an amorphous poly- α -olefin, and most preferably a blend of a semicrystalline propylene homopolymer or copolymer with another poly- α -olefin and an amorphous copolymer or terpolymer of ethylene with another poly- α -olefin or diene. Although any diene is suitable for use in a co- or terpolymer, preferably the diene is ethylidene norbornene, dicyclopentadiene, or hexadiene. The most preferred polyolefin base component includes a semi-crystalline polypropylene blended with an ethylene copolymer of a poly- α -olefin. The term "poly- α -olefin(s)" used in the invention means alkenes of 1 to 20 carbon atoms, preferably 1 to 10 carbon atoms, having a double bond between the first and second carbon atoms. The polyolefin component is a base component, i.e., is the predominant component in the composition, and is not capable of crosslinking under the radiation described herein. This base component is typically present in an amount of about 99 to 55 weight percent of the composition, preferably about 95 to 65 weight percent of the composition, and more preferably about 90 to 70 weight percent of the composition. The polyolefin component, or polyolefin base component, is generally the remainder of the polyolefin composition after the radiation-polymerizable component, photoinitiator and any optional filler are combined.

[0035] The polyolefin of the polyolefin base component is considered semi-crystalline when it has a crystallinity of at least about 30%, while fully crystalline materials, having a crystallinity of from 70 to 100% as determined by X-ray diffraction, are also suitable. When polypropylene is the selected olefin, a degree of crystallinity of between 30 to 98% is acceptable to achieve sufficiently crystalline behavior, although 60 to 70% is preferred, amorphous polyolefins typically have a crystallinity of below 30%. The molecular weight average of the polyolefin is typically between 10'000 and 300'000, more typically between 50'000 and 150'000. Blends of different molecular weight polymers may be utilized, if desired.

[0036] The enhanced surface durability polyolefin composition also includes a radiation-polymerizable component

(b) and a photoinitiator (c). The radiation-polymerizable component (b) is typically an unsaturated polyolefin. The unsaturated polyolefin may be any suitable polyolefin described herein for the polyolefin component, except that it should have at least about one percent of its covalent bonds unsaturated. It is preferred to have greater unsaturation in the radiation-polymerizable component, which results in greater and more rapid crosslinking when exposed to radiation and ultimately enhances the surface characteristics of the polyolefin composition to a greater extent. The unsaturated polyolefin may be, for example, an ethylene, propylene and diene terpolymer; polybutadiene; polyisoprene; a styrenic polymer; or a mixture thereof; or the like. Preferably, however, the radiation-polymerizable component is an ethylene α -olefin copolymer, and more preferably a copolymer of ethylene and propylene. The radiation-polymerizable component is present in an amount sufficient to enhance the surface durability of the polyolefin composition when radiation-cured. The radiation-polymerizable component is preferably present in about 1 to 30 weight percent, more preferably about 5 to 20 weight percent, and most preferably about 10 to 15 weight percent, of the polyolefin composition.

[0037] The polyolefin composition also includes a photoinitiator (c), or free radical initiator, to facilitate curing of the polyolefin composition when irradiated. The photoinitiator may include any compounds capable of initiating free radical cleavage to crosslink the radiation-polymerizable component. Suitable photoinitiators typically include benzoin and benzoin ether derivatives; benzil ketal and its derivatives; α , α -dialkoxycetophenone derivatives; α -aminoalkylketone derivatives; α -hydroxyalkylketone derivatives; mono- or bis- or trisacylphosphine oxides; mono- or bis- or trisacylphosphine sulfides; phenylglyoxylate derivatives; O-acyl-2-oximino ketone derivatives; benzophenone and its derivatives; Michler's ketone and its derivatives; thioxanthone and its derivatives; and all the polymer-bound compounds of the type mentioned above; and the like. Specific photoinitiators can include for example 2,2-dimethoxy-2-phenylacetophenone, bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylphenyl phosphine oxide, bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide, bis(2,4,6-trimethylbenzoyl)-phenyl phosphine oxide, 2,4,6-trimethylbenzoyl-diphenyl phosphine oxide, bis(2,4,6-trimethylbenzoyl)-2,4-dipentoxyphenyl phosphine oxide, 2-benzyl-2-(N,N-dimethylamino)-1-(4-morpholinophenyl)-1-butanone, 2-methyl-1-(4-methylthiophenyl)-2-morpholinopropan-1-one, 2-hydroxy-2-methyl-1-phenyl-propanone and 1-hydroxy-cyclohexylphenyl ketone. Preferred photoinitiators are of the type - benzil ketal derivatives and acylphosphine oxides or a mixture thereof. The photoinitiator is typically present in an amount sufficient to initiate crosslinking of the radiation-polymerizable component when the polyolefin composition is exposed to radiation. Preferably, the photoinitiator is present in an amount of about 0.01 to 5 weight percent, more preferably about 0.05 to 4 weight percent, and most preferably about 0.1 to 3 weight percent, of the polyolefin composition. Preferably, the least amount of photoinitiator necessary to cure the polyolefin composition in a sufficiently rapid manner is employed.

[0038] Fillers (d) may optionally be included within the polyolefin compositions of the present invention. Calcium carbonate, clay, talc, mica, wollastonite, glass, silica, zinc oxide, titanium dioxide, and the like are all suitable fillers for use with the polyolefins. The most appropriate fillers are typically selected depending upon the desired qualities in the final polyolefin products, and selecting such fillers is readily accomplished by one of ordinary skill in the art. The fillers are typically present in an amount of about 1 to 30 weight percent, and preferably between 5 to 15 weight percent, of the polyolefin composition.

[0039] To prepare the polyolefin composition, (a) a polyolefin component, (b) at least one radiation-polymerizable component, (c) at least one photoinitiator, and (d) any optional filler(s) are combined to form a curable composition. The various components are typically mixed and the radiation-polymerizable component, photoinitiator, and polyolefin component are preferably, substantially uniformly dispersed.

[0040] The polyolefin composition can also include one or more stabilizers (e) to impart stability to the composition during mixing, during mechanical processing and during the intended end use application which may include exposure to elevated temperatures or exposure to sunlight or both. The stabilizers of the instant invention may, for example, be selected from the following:

1. Antioxidants

1.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, nonylphenols which are linear or branched in the side chains, for example, 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol and mixtures thereof.

1.2. Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-di-dodecylthiomethyl-4-nonylphenol.

1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydro-

quinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis-(3,5-di-tert-butyl-4-hydroxyphenyl) adipate.

1.4. Tocopherols, for example α -tocopherol, β -tocopherol, γ -tocopherol, δ -tocopherol and mixtures thereof (Vitamin E).

1.5. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis(3,6-di-sec-amyphenol), 4,4'-bis-(2,6-dimethyl-4-hydroxyphenyl) disulfide.

1.6. Alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α -methylcyclohexyl)phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α , α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,1-bis-(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis-(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis-(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra-(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

1.7. O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isooctyl-3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate.

1.8. Hydroxybenzylated malonates, for example dioctadecyl-2,2-bis-(3,5-di-tert-butyl-2-hydroxybenzyl)-malonate, di-octadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)-malonate, di-dodecylmercaptoethyl-2,2-bis-(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, bis[4-(1,1,3,3-tetramethylbutyl)phenyl]-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.

1.9. Aromatic hydroxybenzyl compounds, for example 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.

1.10. Triazine Compounds, for example 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris-(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate.

1.11. Benzylphosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate, the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid.

1.12. Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate.

1.13. Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.14. Esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis-(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.15. Esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)

isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane,

1.16. Esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)-oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.17. Amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)pronionic acid e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hydrazine.

1.18. Ascorbic acid or derivatives, for example, a salt or ester of ascorbic acid, such as ascorbyl palmitate, dipalmitate L-ascorbate, sodium L-ascorbate-2-sulfate, or an ascorbic salt, such as sodium, potassium, and calcium, or mixtures thereof.

1.19. Aminic antioxidants, for example N,N'-di-isopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-bis(2-naphthyl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulfamoyl)diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, for example p,p'-di-tert-octyldiphenylamine, 4-n-butylaminophenol, 4-butyrylaminophenol, 4-nonylamino-phenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, bis(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylaminomethylphenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-bis[(2-methylphenyl)amino]ethane, 1,2-bis(phenylamino)propane, (o-tolyl)biguanide, Bis[4-(1',3'-dimethylbutyl)phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, a mixture of mono- and dialkylated tert-butyl/tert-octyldiphenylamines, a mixture of mono- and dialkylated nonyldiphenylamines, a mixture of mono- and dialkylated dodecyldiphenylamines, a mixture of mono- and dialkylated isopropyl/isohexyldiphenylamines; a mixture of mono- and dialkylated tert-butyl-diphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- and dialkylated tert-butyl/tert-octylphenothiazines, a mixture of mono- and dialkylated tert-octyl-phenothiazines, N-allylphenothiazin, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis-(2,2,6,6-tetramethyl-piperid-4-yl)-hexamethylenediamine, bis(2,2,6,6-tetramethylpiperid-4-yl)sebacate, 2,2,6,6-tetramethylpiperidin-4-one, 2,2,6,6-tetramethylpiperidin-4-ol.

2. UV absorbers and light stabilisers

2.1. 2-(2'-Hydroxyphenyl)benzotriazoles, for example 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chloro-benzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octyloxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2(3',5'-bis-(α,α -dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, mixture of 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)-carbonylethyl]-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole, and 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonylethyl)phenyl)benzotriazole, 2,2'-methylene-bis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazole-2-ylphenol]; the transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonylethyl)-2'-hydroxyphenyl]-2H-benzotriazole with polyethylene glycol 300, where R = 3'-tert-butyl-4'-hydroxy-5'-2H-benzotriazol-2-ylphenyl.

2.2. 2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives.

2.3. Esters of substituted and unsubstituted benzoic acids, as for example 4-tertbutyl-phenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoyl resorcinol, bis(4-tert-butylbenzoyl) resorcinol, benzoyl resorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxy-

benzoate.

2.4. Acrylates, for example ethyl α -cyano- β , β -diphenylacrylate, isooctyl α -cyano- β , β -diphenylacrylate, methyl α -carbomethoxycinnamate, methyl α -cyano- β -methyl-p-methoxy-cinnamate, butyl α -cyano- β -methyl-p-methoxy-cinnamate, methyl α -carbomethoxy-p-methoxycinnamate and N-(β -carbomethoxy- β -cyanovinyl)-2-methylindoline.

2.5. Nickel compounds, for example nickel complexes of 2,2'-thio-bis-[4-(1,1,3,3-tetramethylbutyl)phenol], such as the 1:1 or 1:2 complex, with or without additional ligands such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of the monoalkyl esters, e.g. the methyl or ethyl ester, of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid, nickel complexes of ketoximes, e.g. of 2-hydroxy-4-methylphenyl undecylketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, with or without additional ligands.

2.6. Sterically hindered amines, for example bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(2,2,6,6-tetramethyl-4-piperidyl)succinate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, the condensate of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl)nitritotriacetate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butane-tetracarboxylate, 1,1'-(1,2-ethanediyl)bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearoyloxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl)malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decan-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succinate, the condensate of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-bis(4-n-butylamino-2,2,6,6-tetra-methylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensate of 2-chloro-4,6-di-(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis-(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decan-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidin-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidin-2,5-dione, a mixture of 4-hexadecyloxy- and 4-stearoyloxy-2,2,6,6-tetramethylpiperidine, a condensation product of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, a condensation product of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine as well as 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [136504-96-6]); N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimid, N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimide, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4.5]decan-2,4-dione, a reaction product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro[4.5]decan-2,4-dione and epichlorohydrin.

2.7. Oxamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-diethoxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butoxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butoxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-dimethylaminopropyl)oxamide, 2-ethoxy-5-tert-butyl-2'-ethoxanilide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butoxanilide and mixtures of ortho- and para-methoxy-disubstituted oxanilides and mixtures of o- and p-ethoxy-disubstituted oxanilides.

2.8. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[4-(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2,4,6-tris[2-hydroxy-4-(3-butoxy-2-hydroxy-propoxy)phenyl]-1,3,5-triazine, 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine.

3. Metal deactivators, for example N,N'-diphenyloxamide, N-salicylal-N'-salicyloyl hydrazine, N,N'-bis(salicyloyl)hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)oxalyl dihydrazide, oxanilide, isophthaloyl dihydrazide, sebacoyl bisphenylhydrazide, N,N'-diacetyladiopoyl dihydrazide, N,N'-bis(salicyloyl)oxalyl dihydrazide, N,N'-bis(salicyloyl)thiopropionyl dihydrazide.

4. Phosphites and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite,

tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)-pentaerythritol diphosphite, diisodecyloxy-pentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)-pentaerythritol diphosphite, bis(2,4,6-tris(tert-butylphenyl)-pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylene diphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-di-benz[d,g]-1,3,2-dioxaphosphocin, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl)methylphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)ethylphosphite.

5. Hydroxylamines, for example, N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-dioctylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-ditetradecylhydroxylamine, N,N-dihexadecylhydroxylamine, N,N-dioctadecylhydroxylamine, N-hexadecyl-N-octadecylhydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

6. Nitrones, for example, N-benzyl-alpha-phenyl-nitrone, N-ethyl-alpha-methyl-nitrone, N-octyl-alpha-heptyl-nitrone, N-lauryl-alpha-undecyl-nitrone, N-tetradecyl-alpha-tridecyl-nitrone, N-hexadecyl-alpha-pentadecyl-nitrone, N-octadecyl-alpha-heptadecyl-nitrone, N-hexadecyl-alpha-heptadecyl-nitrone, N-octadecyl-alpha-pentadecyl-nitrone, N-heptadecyl-alpha-heptadecyl-nitrone, N-octadecyl-alpha-hexadecyl-nitrone, nitrone derived from N,N-dialkyl-hydroxylamine derived from hydrogenated tallow amine.

7. Thiosynergists, for example, dilauryl thiodipropionate or distearyl thiodipropionate.

8. Peroxide scavengers, for example esters of β -thiodipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl esters, mercaptobenzimidazole or the zinc salt of 2-mercaptobenzimidazole, zinc dibutyldithiocarbamate, dioctadecyl disulfide, pentaerythritol tetrakis(β -dodecylmercapto)propionate.

9. Basic co-stabilisers, for example, melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali metal salts and alkaline earth metal salts of higher fatty acids for example calcium stearate, zinc stearate, magnesium behenate, magnesium stearate, sodium ricinoleate and potassium palmitate, antimony pyrocatecholate or tin pyrocatecholate.

10. Other additives, for example, plasticisers, lubricants, emulsifiers, pigments, rheology additives, catalysts, flow-control agents, optical brighteners, flameproofing agents, antistatic agents and blowing agents.

11. Benzofuranones and indolinones, for example those disclosed in US-A-4325863, US-A-4338244, US-A-5175312, US-A-5216052, US-A-5252643, DE-A-4316611, DE-A-4316622, DE-A-4316876, EP-A-0589839 or EP-A-0591102 or 3-[4-(2-acetoxyethoxy)phenyl]-5,7-di-tert-butyl-benzofuran-2-one, 5,7-di-tert-butyl-3-[4-(2-stearoyloxyethoxy)phenyl]benzofuran-2-one, 3,3'-bis[5,7-di-tert-butyl-3-(4-[2-hydroxyethoxy]phenyl)benzofuran-2-one], 5,7-di-tert-butyl-3-(4-ethoxyphenyl)benzofuran-2-one, 3-(4-acetoxy-3,5-dimethylphenyl)-5,7-di-tert-butylbenzofuran-2-one, 3-(3,5-dimethyl-4-pivaloyloxyphenyl)-5,7-di-tert-butyl-benzofuran-2-one.

[0041] The concentration of the costabilizer in the thermoplastic polyolefin composition is usually from 0.1 to 5 percent by weight of the composition.

[0042] The polyolefin composition is then preferably formed into a desired product by a variety of conventional means, such as injection molding, coinjection molding, blow molding, extrusion, and the like. One of ordinary skill in the art can envision a broad array of useful, desired products easily manufactured by the present invention, including electrical components such as electrode manufacture or insulation, surface treatment of a variety of materials, and automotive parts. A variety of applications may be useful just in the automotive field, although they apply to a variety of other fields of endeavor. It is clear that interior and exterior automotive applications such as instrument panels, thermoformed skins, bumper fascia, claddings, and other interior and exterior trim components can be readily produced with superior durability due to the present invention.

[0043] The polyolefin composition in its uncured state is cured by subjecting the composition to irradiation. The radiation-polymerizable component crosslinking is initiated by a source of ionizing radiation capable of producing free radicals, such as gamma, UV, electron beam, visible, microwave, or infrared radiation. More than one type of radiation may be used, although this is typically avoided due to cost considerations. Preferably, UV or electron beam radiation is used for the curing process.

[0044] For example, when UV radiation is used as the radiation source, the curing process requires at least one UV lamp that directs UV light onto the formulated product. These UV lamps may provide either arc light, which includes a medium pressure mercury lamp and a high pressure xenon lamp, or laser light. The photoinitiator or photoinitiator mixture used must have an absorption spectrum that at least partially overlaps with the emission spectrum of the UV lamp, such that the photoinitiator is capable of absorbing the UV energy. The photoinitiator rapidly initiates a chemical reaction that quickly converts the resin, or radiation-polymerizable component, into a cured (crosslinked) form. This photoinitiated curing typically occurs in less than one second, although this will depend on the rate of UV energy transfer. The UV energy for example has a wavelength of between about 200 to 600 nm, e.g. 300 to 500 nm, preferably 300 to 400 nm. The radiation source suitable to irradiate the compositions according to the invention typically provides energy at a rate of about 0.1 J/cm² and above, for example 0.1-15 J/cm², e.g. 1-15 J/cm², or 2-15 J/cm², or 1-6 J/cm². For

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example, a lamp of about 1-6 J/cm² would typically take less than one second to cure a thermoplastic polyolefin composition. It of course is possible for other cure mechanisms (such as thermal or moisture induced curing) to continue well after photoinitiated crosslinking is complete.

[0045] A test was developed by Solvay Engineered Polymers to measure relative surface scratch resistance. For this test, the test specimens are at least 4" x 4" (100 mm x 100 mm) in dimensions, with a hole drilled in the middle for mounting. A Taber Abrasion test machine (described further in ASTM D1044) was modified by substituting a stainless steel slider with a sharp tip (radius = 0.25 mm) in place of the sanding wheels to scratch the surface of the specimens. With the tip offset 34 mm from the center of rotation and the turntable spinning at 72 rpm, the actual sliding velocity is equal to 25 mm/sec, which is similar to the condition of someone scratching a surface at normal speed with a fingernail. The test is terminated after one single revolution. The normal load used for this test is 1 lb (453.6 g). Upon completion of the test, the specimens are then rated visually on a numerical scale of 1 to 5 (1 = excellent, hardly any marring is visible; 5 = badly scratched). The width of the wear track and the characteristics of the failure surface can also be further studied with an optical microscope or more sophisticated instruments such as surface profilometer and scanning force microscope. The typical dimensions of the wear paths corresponding to the mar ratings are as follows:

| Mar Rating | Width of Scratch (μm) | Relative Performance |
|------------|-----------------------|----------------------|
| 1 | <50 | Excellent |
| 1.5 | 50 --- 200 | Very good |
| 2 | 200 --- 300 | Good |
| 3 | 300 --- 400 | Fair |
| 4 | 400 --- 500 | Bad |
| 5 | > 500 | Poor |

[0046] A value of 1.5 or less in this test is indicative of very good or excellent performance.

[0047] The invention is further defined by reference to the following examples describing in detail the preparation of the compositions of the present invention. It will be apparent to those of ordinary skill in the art that many modifications, both to materials and methods, may be practiced without departing from the purpose and intent of this invention.

Photoinitiator A is 2,2-dimethoxy-2-phenylacetophenone.

Photoinitiator B is 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one.

Examples 1-2: UV irradiation with and without photoinitiator

[0048] Examples 1-2, set forth in Table I below, compare samples of polyolefin component and radiation-curable component both with and without a photoinitiator that are subjected to UV radiation by a mercury lamp. The formulation with photoinitiator shows significant increase in Shore hardness upon irradiation, whereas the formulation without photoinitiator shows no change in Shore hardness. After soaking both formulations in xylene for four hours, the sample with photoinitiator also shows less weight increase, indicating there is crosslinking on the surface that is slowing down the diffusion of xylene into the 5 sample plaque. The feasibility of the UV curing process is thus confirmed.

[0049] Determination of Shore hardness according to DIN 53505; of Rockwell hardness according to ASTM D 785. The higher the "Shore" and "Rockwell" values the harder is the cured formulation.

[0050] The determination of the values of the Solvay scale is described above. The lower the value, the harder is the cured formulation.

Table I:

| Indication of crosslinking via UV-curing | | |
|--|---------------------|-----------|
| | Example 1 (Control) | Example 2 |
| Composition (wt %): | | |
| Polypropylene ¹ | 30 | 28.8 |
| Polybutadiene ² | 69.8 | 67 |
| Photoinitiator A | 0 | 4 |

Notes: ¹ isotactic polypropylene. $M_w = 240,000$; $M_w/M_n = 4.1$;

² amorphous cis-1,4-polybutadiene, Mooney Viscosity ML(1+4, 100C) = 40.

Table I: (continued)

| Indication of crosslinking via UV-curing | | |
|--|---------------------------|---------------------------|
| | Example 1 (Control) | Example 2 |
| Antioxidant ³ | 0.2 | 0.2 |
| Irradiation Source: | Mercury Lamp (H bulb) | Mercury Lamp (H bulb) |
| Atmosphere: | Nitrogen | Nitrogen |
| Irradiation Level: | 2 and 4 J/cm ² | 2 and 4 J/cm ² |
| Results: | | |
| Shore "A" | | |
| (0 J/cm ²) | 87 | 86 |
| (2 J/cm ²) | 88 | 89 |
| (4 J/cm ²) | 90 | 95 |
| Shore "D" | | |
| (0 J/cm ²) | 25 | 21 |
| (2 J/cm ²) | 24 | 26 |
| Weight Increase after 4-hr Xylene Soak | | |
| (2 J/cm ²) | 104% | 89% |
| (4 J/cm ²) | 96% | 59% |

³ antioxidant - 1:1 tetrakis[methylene(3,5-di-tert-butyl-4-hydroxy-hydrocinnamate)]methane / tris(2,4-di-tert-butylphenyl)phosphite

Examples 3-5: Surface characteristics based on photoinitiation

[0051] Examples 3-5, set forth in Table II below, compare the surface hardness and mar resistance performance of representative engineered polyolefin blends before and after photoinitiation. In this experiment, a mercury "D" bulb is used as a radiation source. This bulb has lower emissions at short wavelengths and enhanced emissions at longer wavelengths when compared to the mercury "H" bulb. Examples 4 and 5, using photoinitiator "A" and photoinitiator "B" respectively, exhibit significantly bigger increases in hardness and much improved mar resistance than the sample without photoinitiator in Example 3.

Table II:

| Improvement of Surface Durability through a Mercury Lamp UV-Curing Process | | | |
|--|--|-----------|-----------|
| | Example 3 (control) | Example 4 | Example 5 |
| Composition (wt %) | | | |
| Polypropylene ¹ | 69.8 | 67.8 | 67.8 |
| Poly(ethylene-co- α -olefin) ² | 15 | 15 | 15 |
| Methacrylated Polybutadiene ³ | 15 | 15 | 15 |
| Photoinitiator A | 0 | 2 | 0 |
| Photoinitiator B | 0 | 0 | 2 |
| Antioxidant ⁴ | 0.2 | 0.2 | 0.2 |
| Irradiation Source: | <==== Mercury Lamp with "D" Bulb =====> | | |
| Atmosphere: | <=====Air=====> | | |
| Irradiation Energy: | <=====Two levels: 2.7 and 5.5 J/cm ² =====> | | |
| Test Results after UV-cure: | | | |

Note: ¹ isotactic polypropylene. $M_w = 240,000$; $M_w/M_n = 4.1$;

² poly(ethylene-co-octene); $M_w = 100,000$; $M_w/M_n = 2$;

³ methacrylated polybutadiene, Brookfield viscosity = 60'000 cps @35°C; 15% acrylate content.

⁴ antioxidant = 1:1 tetrakis[methylene (3,5-di-tert-butyl-4-hydroxy-hydrocinnamate)] methane / tris(2,4-di-tert-butylphenyl) phosphite.

Table II: (continued)

| Improvement of Surface Durability through a Mercury Lamp UV-Curing Process | | | |
|--|------------------------|-----------|-----------|
| | Example 3 (control) | Example 4 | Example 5 |
| Shore "D" | | | |
| (0 J/cm ²) | 66 | 65 | 65 |
| (2.7 J/cm ²) | 67 | 68 | 69 |
| (5.5 J/cm ²) | 67 | 69 | 70 |
| Rockwell "R" | | | |
| (0 J/cm ²) | 72 | 68 | 68 |
| (2.7 J/cm ²) | 72 | 73 | 76 |
| (5.5 J/cm ²) | 73 | 75 | 80 |
| Scratch Rating (Solvay Test*) | | | |
| (0 J/cm ²) | 3.5 | 3.5 | 3.5 |
| (2.7 J/cm ²) | 2.5 | 2.5 | 3.0 |
| (5.5 J/cm ²) | 3.0 | 1.5 | 2.0 |

Examples 6-9: Radiation-curable components having greater unsaturation

[0052] Examples 6-9, set forth in Table III below, are prepared such that the radiation-polymerizable component has higher unsaturation (more methacrylate-grafted polybutadiene) when compounded and compared with the formulations in Table II (Examples 3-5). The mar resistance of Examples 6-9 after UV curing shows further improvement over the polyolefin composition with less unsaturation in the radiation-polymerizable component.

Table III:

| Surface modification with photoinitiators and UV-curing | | | | |
|---|---|-----------|-----------|-----------|
| | Example 6 | Example 7 | Example 8 | Example 9 |
| <i>Composition (wt%):</i> | | | | |
| Polypropylene ¹ | 67.8 | 67.8 | 67.8 | 67.8 |
| Poly(ethylene-co- α -olefin) ² | 15 | 10 | 15 | 10 |
| Polybutadiene-g-methacrylate ³ | 15 | 20 | 15 | 20 |
| Photoinitiator A | 2 | 2 | 0 | 0 |
| Photoinitiator B | 0 | 0 | 2 | 2 |
| Antioxidant ⁴ | 0.2 | 0.2 | 0.2 | 0.2 |
| <i>Irradiation Source:</i> | <===== Mercury Lamp with "D" Bulb =====> | | | |
| <i>Atmosphere:</i> | <===== Air =====> | | | |
| <i>Irradiation Energy:</i> | <===== Two levels: 2.7 and 5.5 J/cm ² =====> | | | |
| <i>Test Results after UV-cure:</i> | | | | |
| Shore "D" | | | | |
| (0 J/cm ²) | 65 | 65 | 65 | 65 |
| (2.7 J/cm ²) | 68 | 68 | 69 | 67 |
| (5.5 J/cm ²) | 69 | 69 | 70 | 68 |

Note: ¹ isotactic polypropylene. $M_w = 240,000$; $M_w/M_n = 4.1$;

² poly(ethylene-co-octene); $M_w = 100,000$; $M_w/M_n = 2$;

³ methacrylated polybutadiene, Brookfield viscosity = 60,000 cps @ 35°C; 15% acrylate content.

⁴ antioxidant = 1:1 tetrakis[methylene(3,5-di-tert-butyl-4-hydroxy-hydrocinnamate)] methane / tris(2,4-di-tert-butylphenyl) phosphite.

Table III: (continued)

| Surface modification with photoinitiators and UV-curing | | | | |
|---|-----------|-----------|-----------|-----------|
| | Example 6 | Example 7 | Example 8 | Example 9 |
| Rockwell "R" | | | | |
| (0 J/cm ²) | 69 | 64 | 68 | 62 |
| (2.7 J/cm ²) | 73 | 76 | 76 | 77 |
| (5.5 J/cm ²) | 75 | 79 | 80 | 80 |
| Scratch Rating (Solvay) | | | | |
| (0 J/cm ²) | 3.5 | 4.0 | 3.5 | 4.0 |
| (2.7 J/cm ²) | 2.5 | 2.0 | 4.0 | 2.5 |
| (5.5 J/cm ²) | 1.5 | 1.5 | 2.0 | 1.5 |

Example 10: Effect of UV radiation and thermal treatment on surface durability

[0053] Example 10, set forth in Table IV below, is prepared to examine the effect of treating the plastic component with UV radiation followed by a thermal cure. The formulation when exposed to UV radiation and a subsequent thermal treatment results in a surface with improved mar resistance compared with a plastic component which is exposed to the same UV irradiation but without the thermal cure.

Table IV:

| Effect of UV radiation and thermal curing | |
|---|----------------------------|
| | Example 10 |
| <i>Composition (wt%):</i> | |
| Polypropylene ¹ | 68.4 |
| Polybutadiene-g-methacrylate ² | 29.4 |
| Photoinitiator B | 2.0 |
| Antioxidant ³ | 0.2 |
| <i>Irradiation Source:</i> | Mercury Lamp with "D" Bulb |
| <i>Atmosphere:</i> | Air |
| <i>Irradiation Energy:</i> | 10.8 J/cm ² |
| <i>Thermal Cure:</i> | 80 °C / 2 hours |
| <i>Test Results after UV-cure:</i> | |
| Scratch Rating (Solvay) | |
| (0 J/cm ²) | 5.0 |
| (10.8 J/cm ²) | 1.5 |
| (10.8 J/cm ² + 80 °C / 2 hours) | 1.0 |

Note: ¹ isotactic polypropylene. $M_w = 240,000$; $M_w/M_n = 4.1$;

² methacrylated polybutadiene. Brookfield viscosity = 60,000 cps @ 35°C; 15% acrylate content.

³ antioxidant = 1:1 tetrakis[methylene (3,5-di-tert-butyl-4-hydroxy-hydrocinnamate)] methane / tris(2,4-di-tert-butylphenyl) phosphite.

EXAMPLE 11: Incorporation of Stabilizers

[0054] Articles prepared according to Example 10 which additionally contain a hindered amine with a molar mass less than 2000, preferably a hindered amine with a molecular weight between 400 - 1000, a hindered amine with a molar mass greater than 2000, preferably a hindered amine with a molecular weight between 2000 - 4000, a UV absorber of the hydroxyphenyl benzotriazole class or mixtures thereof, exhibit improved mar resistance and stability against the deleterious effects of UV light and thermal exposure.

[0055] Although preferred embodiments of the invention have been described in the foregoing description, it will be understood that the invention is not limited to the specific embodiments disclosed herein but is capable of numerous modifications by one of ordinary skill in the art. It will be understood that the materials used and the chemical details

may be slightly different or modified without departing from the methods and compositions disclosed and taught by the present invention.

Claims

1. A thermoplastic polyolefin composition having enhanced surface durability comprising:
 - (a) a base component of a thermoplastic polyolefin;
 - (b) at least one radiation-polymerizable component; and
 - (c) at least one photoinitiator.
2. A composition according to claim 1 which further comprises a filler (d) in an amount of 0.1 to 30 percent by weight.
3. A composition according to claim 1 wherein the thermoplastic polyolefin base component (a) comprises a blend of crystalline or semi-crystalline poly- α -olefin and an amorphous poly- α -olefin.
4. A composition according to claim 1 wherein the thermoplastic polyolefin base component (a) is present in an amount of 99 to 55 weight percent of the composition.
5. A composition according to claim 1 wherein the radiation polymerizable component (b) comprises an unsaturated polyolefin
6. A composition according to claim 5 wherein the unsaturated polyolefin (b) comprises ethylene/propylene/diene copolymer; polybutadiene; polyisoprene; a styrenic polymer; an ethylene/propylene copolymer; or mixtures thereof.
7. A composition according to claim 1 wherein the radiation polymerizable base component (b) is present in an amount of 1 to 30 percent by weight of the thermoplastic polyolefin composition.
8. A composition according to claim 1 wherein the photoinitiator (c) is present in an amount of 0.01 to 5 percent by weight of the composition.
9. A method of providing a cured thermoplastic polyolefin composition having enhanced surface durability which comprises:
 - (1) preparing a mixture comprising
 - (a) a thermoplastic polyolefin base component,
 - (b) at least one radiation-polymerizable component; and
 - (c) at least one photoinitiator; and
 - (2) exposing a surface of the thermoplastic polyolefin composition to radiation, thereby providing a thermoplastic polyolefin composition having enhanced surface durability.
10. A method according to claim 9 wherein the radiation is selected to be ultraviolet, electron beam, gamma, visible, microwave, infrared or thermal radiation, or mixtures thereof.
11. A method according to claim 10 wherein the radiation is imparted at a power of 0.1 J/cm² and above and at a wavelength between 200 and 500 nm.
12. A method according to claim 9 wherein the thermoplastic polyolefin base component (a) is selected to be a blend of a crystalline or semi-crystalline poly- α -olefin and an amorphous poly- α -olefin, the radiation-polymerizable component (b) is selected to be an unsaturated polyolefin that is present in an amount of 0.01 to 20 percent by weight of the composition, the photoinitiator (c) is 2,2-dimethoxy-2-phenylacetophenone or 2-methyl-1-(4-methylthiophenyl)-2-morpholino-propan-1-one or a mixture of bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide and 1-hydroxy-cyclohexylphenyl ketone that is present in an amount of 0.1 to 5 percent by weight of the composition, and optionally a filler (d) is added to the mixture.

13. A method according to claim 9 which further comprises forming the thermoplastic polyolefin composition into a desired shape prior to exposing the surface of the composition to the radiation.

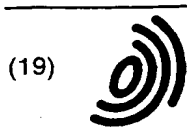
14. A thermoplastic polyolefin composition having enhanced surface durability which is formed by the method according to claim 9.

15. A thermoplastic polyolefin composition according to claim 1 wherein the radiation-polymerizable component (b) is polymerized to provide enhanced surface durability with an outer surface of the composition containing a sufficient amount of the polymerized component to provide a scratch rating of two or lower on the Solvay scale.

16. A composition according to claim 1 which additionally contains at least one stabilizer (e) selected from the group consisting of the phenolic antioxidants, the phosphites, the hydroxylamines, the hindered amines, the UV absorbers and combinations thereof.

17. A method according to claim 9 wherein the composition additionally contains at least one stabilizer (e) selected from the group consisting of the phenolic antioxidants, the phosphites, the hydroxylamines, the hindered amines, the UV absorbers and combinations thereof.

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(71) Applicants:
• Ciba Specialty Chemicals Holding Inc.
4057 Basel (CH)
• Solvay Engineered Polymers
Grand Prairie, TX 75050 (US)

(72) Inventors:
• Lau, Edmund Kwok-Leung
Arlington TX 76006 (US)
• Srinivasan, Satchit
Carrollton TX 75007 (US)

- Perron, Peter James
Arlington, TX 76006 (US)
- Solera, Peter Shelsey
Suffern NY 10901 (US)
- Debellis, Anthony David
Garnerville NY 10923 (US)
- Chang, Chia-Hu
West Nyack NY 10994 (US)
- Capocci, Gerald Anthony
Greenwich CT 06831 (US)
- Puglisi, Joseph Steven
Ossining NY 10562 (US)
- Horsey, Douglas Wayne
Briarcliff Manor NY 10510 (US)

(74) Representative: Richter, Helmut, Dr. et al
Ciba Specialty Chemicals Holding Inc.,
Patentabteilung,
Klybeckstrasse 141
4057 Basel (CH)

(54) Polyolefin materials having enhanced surface durability and methods of making the same by exposure to radiation

(57) The invention relates to thermoplastic polyolefin compositions having enhanced surface durability and products thereof which include a thermoplastic polyolefin base component at least one radiation-polymerizable component present in an amount sufficient to enhance the surface durability of the thermoplastic polyolefin component when radiation-cured and at least one photoinitiator present in an amount sufficient to initiate crosslinking of the radiation-polymerizable component

upon exposure of the thermoplastic polyolefin composition to radiation. The invention further relates to methods of providing a cured thermoplastic polyolefin composition having enhanced surface durability by preparing a mixture having a thermoplastic polyolefin base component, at least one radiation-polymerizable component, and at least one photoinitiator, and then exposing the thermoplastic polyolefin composition to radiation thereby providing a thermoplastic polyolefin composition having enhanced surface durability.

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EUROPEAN SEARCH REPORT

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| Place of search THE HAGUE | | Date of completion of the search 5 July 1999 | Examiner Clemente Garcia, R |
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